Low Emissivity Coatings for use at High Temperatures

by
B. A. Macklin and J. C. Withers
American Machine & Foundry Company

1. Introduction

The high velocities of aerospace vehicles causes them to attain high skin temperatures both within the earth's atmosphere and upon reentry into the atmosphere. Furthermore, outside the earth's atmosphere, the operating temperatures of propulsion systems generate heat. The results of this heat generated by flight is to place strenuous temperature requirements upon materials which are used for instruments housed within a space vehicle. A problem then exists of how to prevent heat transfer from hot components of an aerospace vehicle to instrument systems within the vehicle.

In an enclosed system such as the interior of a rocket, thermal radiation is the primary process by which heat is transferred to internal systems which have little or no physical contact with the sides of the rocket. The prevention of heat transfer by radiation may be accomplished in two ways.

(1) A material with high absorbity and low thermal conduction could be placed between the hot surface and the surface to be protected, or

(2) A thin low emittance or high reflecting coating may be used to reflect the radiation, thereby reducing the amount of heat absorbed by the surface and maintaining the surface at a lower temperature.

In many aerospace applications weight and space factors are a consideration. Most thermal insulating material which reduces heat transfer to any appreciable extent are either bulky or heavy or both. Insulating materials thus have limited utility in the problem of preventing heat transfer from hot surfaces to systems enclosed by these surfaces.

A low emittance coating however, can reduce heat transfer while at the same time adding only a small amount of weight to a system.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **1960**	2. REPORT TYPE	3. DATES COVERED **00-00-1960 to 00-00-1960**

4. TITLE AND SUBTITLE **Low Emissivity Coatings for Use at High Temperatures**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Wright Air Development Center,Wright Patterson AFB,OH,45433**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**10**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Before considering the manner in which low emittance coatings reduce heat transfer, it will be useful to define some radiation terminology.

Thermal emission is the act or process by which radiant energy is emitted by a body as a consequence of its temperature only.

Emittance is a property of a specimen, it is the ratio of its rate of emission of radiant energy to that of a black body radiator at the same temperature, under the same conditions.

Emissivity is the limiting case of emittance. It is the emittance of a specimen which is optically smooth and opaque.

A low emittance coating serves to reduce heat transfer by two phenomena. First, if a low emittance coating is applied to a hot surface at a specified temperature, the amount of energy radiated at this temperature is reduced in direct proportion to the emittance of the applied material. The lower the emittance of the coating material, the lower is the amount of radiation. The manner in which this reduction in radiated energy occurs can be shown by the Stefan-Boltzman Law

$$W = \epsilon_t \sigma T^4$$

where W is total radiant flux from the surface
ϵ_t is the total emittance of the material
and T^4 is the absolute temperature to the fourth power.

The second way by which a low emittance coating can serve to reduce heat transfer is through reflection of incident radiation. In this case however, the low emittance coating is applied to the system to be protected. The manner in which heat reflection occurs can be seen by considering the relationship which exists between the radiant flux or emittance from a substance and its absorptance for radiation.

$$\frac{W}{\alpha} = W_{BB}$$

This relationship states that at a given temperature the radiant flux, W, from any nonblackbody radiator divided by is absorbance, α, for blackbody radiation at the same temperature is equal to the radiant flux, W_{BB}, from a black body. By substituting with the Stefan-Boltzman Law for W and W_{BB} we get the relation that

$$\epsilon_t = \alpha_t$$

The emittance is equal to the absorbance. Since, for an opaque body, any radiant energy striking the surface of the body will be partially reflected and partially absorbed ($W_{incident} = W_i r + W_i \alpha$), it can be seen that $r = 1 - \epsilon$. The smaller the emittance, the higher the reflectance.

2. Materials

Bearing in mind that a low emittance coating can reduce heat transfer through reducing thermal radiation $W = \epsilon \sigma T^4$ and that a low emittance coating can reduce heat transfer through reflection, $R = 1 - \epsilon$, let us consider what materials are available for high temperature low emittance coatings. Before doing this however, we should specify the temperature range and low emittance values of interest. At AMF we have been primarily concerned with low emittance materials which have an emittance of 0.1 or less and which can be used in the 300°C to 1000°C temperature range. The choice of emittance values of less than 0.1 is rather arbitrary because the particular emittance values desired in any application depends on the amount of heat involved. However, in all of our applications we have sought a coating with the lowest emittance possible. The temperature to which the coating will be used of course depends upon whether the coating will be used as a reflector or a low emitter. However, the majority of high temperature materials on which a low emittance coating will be used are not used at temperatures above 1000°C.

Table 1 shows all the metals which have the desired low emittance property and can withstand the temperatures up to 1000°C without melting. From this number of materials it would appear that selecting low emittance materials for use at high temperatures would be no problem; however, factors other than emittance must be considered.

Oxidation Resistance. Emittance is not a surface property of a material alone, however, the surface condition does have an important effect upon the emittance of a material. The surface functions to determine what fraction of radiant energy incident upon it is reflected and what portion of energy is refracted and passes through it. The surface function is the same whether the radiation is incident upon the surface from within as in the case of radiation emitting from a substance as a result of its temperature or whether the radiation is incident upon the surface from outside.

That is, the surface of a material has the same effect on radiant energy as a glass surface has on visible light when the light passes from air into glass and is refracted or vice versa.

TABLE 1

Total Normal Emissivity of Low Emissive Metals

Metal	Melting Point	Oxidation Resistance	Temperature °C 25°C	100°C	500°C	1000°C
Copper	1083	Poor	.02	.03	.04	.07
Iron	1535	Poor	.05	.05	.06	.08
Nickel	1455	Poor	.048	.06	.07	0.1
Palladium	1549	Good	.03	0.03	0.060	0.12
Rhodium	1966	Good	0.03	0.038	0.050	0.084
Silver	960	Good, but tarnishes	0.02	.025	..03	---
Gold	1063	Good	0.02	.03	.03	.03
Platinum	1773	Good	0.03	0.047	0.096	0.15

Obviously then if the surface of a metal oxidizes this will change the emittance properties of the metal. In the case of low emittance material the oxidation always results in an increase in emittance. For example clean polished copper has an emittance of .02 to .03 in the temperature range 300°C to 1000°C. Whereas oxidized copper has an emittance of 0.15 to 0.25 in the same temperature range. This means that any metal to be useful as a low emittance coating against heat transfer must be oxidation resistant or must be protected from oxidation.

At present no materials are known which can both protect a metal from oxidation at elevated temperatures and are sufficiently transparent to radiant energy. The requirement of oxidation resistance thus in effect eliminates as high temperature low emittance coatings the use of all metals except gold, rhodium, and platinum.

Application of Coating. Another consideration in the choice of materials for forming low emittance coatings is the method of application. As mentioned the surface condition has a large effect on the emittance of a material. The smoother the surface the lower the emittance. Several methods of application are considered best for forming the type of surface with the lowest emittance. These methods are vacuum evaporation, thermal decomposition of resinate solutions, vapor plating, cladding, electroplating, and cathode sputtering. The choice of which method to use depends upon the particular low emittance material under consideration, geometry of substrate, thickness of coating, etc.

Experimental Work at AMF. At AMF we are currently experimenting with a number of low emittance materials for reducing heat transfer through lowering the amount of energy radiated. That is to say the emittance coatings will be applied to the hot surface and lower its emittance.

To show an example of how a low emissive coating may be applied to a hot surface and lower its radiation, the problem of maintaining a cooled instrument package inside a nose cone may be considered. This problem is being investigated at AMF. The equation for computing the net interchange between two isothermal zones, which are the inside of the nose cone and the instrument package separated by air, is

$$q_{1-2} = \sigma A_1 f_{1-2} (T_1^4 - T_2^4).$$

The variable f_{1-2} is a function of the emissivities and absorptivities of surfaces A_1 and A_2 and of the geometric configuration factors in which A_1 and A_2 are involved. However, if the inside of the nose cone is considered to be a black body irradiator and the distance between the nose cone and the instrument package is relatively small, the following relation gives a close approximation of the condition

$$\frac{dQ}{dt} = \sigma\epsilon\, A\,(Ta^4 - Ts^4)$$

where σ = black body constant (Stefan-Boltzman)
ϵ = emissivity
A = area
Ta = ambient temperature inside the nose cone
Ts = temperature of the skin of the instrument package.

The emissivity characteristics of the interior of the nose cone determine the rate at which heat is radiated to the instrument package. If the emissivity of the inside of the nose cone is decreased it will limit the rise of the interior temperature due to a decrease in radiation.

In terms of black body equivalent for the description of the radiation from a surface at high temperature (the inside of a nose cone) the equation may be written

$$\frac{dQ}{dt} = \sigma\epsilon\, A\, Ts^4$$

where the temperature of the surroundings has been neglected. In order to find the black body equivalent temperature to provide the rate of heat transfer, the equation may be written

$$\frac{dQ}{dt} = \sigma A(\epsilon^{1/4}\, Ts)^4.$$

In comparison with the black body radiator the following equation may be rather

$$\frac{dQ}{dt} = \sigma A\, T^4.$$

Combining the equations, the equivalent black body temperature is $T = \epsilon^{1/4}\, Ts$. Now suppose the skin temperature of the inside of the nose cone is at 850°F. If the inside of the nose cone is coated with a 0.03 emissivity coating (gold), the equivalent black body temperature of the inside of the nose cone reduces to $T = (0.03)^{1/4}\,(727^{\circ}K) = 303^{\circ}K = 86^{\circ}F$. It is thus seen that the power of the inside surface of the nose cone at 850°F (727°K) as a radiator has been reduced to an equivalent black body radiation at 303°K (86°F) if it is coated with 0.03

emissivity coating, as an example, gold. Thus by coating both the hot surface, the radiator (in this case the inside of a nose cone) with a low emissivity coating and the instrument package with a low emissivity coating to reflect the radiation, the inside of the package is maintained at temperature only slightly above room temperature. In our present work with Mr. Van Vliet we are trying to develop a coating with the lowest possible emittance for use up to 800°C. For this reason we are giving special consideration to the use of gold as a low emittance coating. Gold is especially well suited for this application because of its low emittance, .03 up to 1000°C and its resistance to oxidation at elevated temperatures. Additionally gold also can be applied as smooth bright coatings by all of the methods mentioned earlier, vacuum evaporation, thermal decomposition of gold resinate solutions, electroplating, cladding, vapor plating, and sputtering. In most of our experimental work we have used Inconel X as a base material upon which gold is applied by evaporation and thermal decomposition of resinates. Inconel X is a high nickel (80%) alloy which is fairly representative of high temperature alloys.

"Figure 1 shows the emittance of two types of gold coatings applied onto Inconel X. The difference in the emittance values between the different gold coatings is attributed to the surface conditions of the gold produced by the application procedure. Also the liquid bright gold contains small amounts of impurities which were added to promote adhesion and resulted in an increase in the emissivity. It can be seen from Figure 1 that evaporated gold gives the lowest emittance coating, however liquid bright gold is still in the range of usefulness."

The major problem associated with the use of gold as a high temperature, low emittance coating is that at temperatures slightly above ambient, it readily diffuses with practically all base materials. This diffusion is a very serious problem and a major effort is being expended to retard the diffusion into the base material. The seriousness of the diffusion of gold can be shown by the change in emittance of gold on Inconel X when heated to 800°C in air. The measured total normal emissivity of evaporated gold on Inconel X at 300°C is 0.03. This value is approximately five minutes after the sample was heated from room temperature to 300°C. A second sample treated in an analogous manner heated to 800°C had an emissivity of 0.045. After the sample had remained at 800°C for 15 minutes the emissivity had dropped to 0.24 which was a result of the diffusion of gold into the Inconel.

The approach being investigated to stop the diffusion of gold into the substrate is to impose a diffusion barrier between gold and Inconel X. The selection of materials to test for diffusion barriers was based on the following facts about diffusion.

(1) The diffusivity of a given element is usually smaller the higher the melting point of the solvent.

(2) The diffusivity depends inversely upon the solid solubility, being usually greatest for elements which are only slightly soluble and

least for elements which have a wide solubility range.

(3) For mutual diffusion of two metals the direction of most rapid diffusion is in the direction of the metal with the greater interatomic distance.

Using these observations these types of materials were selected for study as diffusion barriers. These materials are characterized as follows.

(1) Ceramic coatings. The purpose of a ceramic coating as a diffusion barrier would be to increase the melting point of the solvent or base into which the gold can diffuse. Both silica and phosphate base ceramics are being tested. Presently primary emphasis is being placed on NBS A418 glass as a diffusion barrier. Preliminary results indicate that A418 is an excellent diffusion barrier for gold and Inconel X.

k(2) Oxides with small interatomic spacing than Inconel X and gold. One oxide being tested is silicon monoxide. The method of application is by vacuum deposition.

"To determine the effectiveness of these materials as diffusion barriers for gold at 800°C we measured the rate of increase of emittance of gold coatings on the materials at 800°C. This procedure is a good indication of the relative rate that gold is diffusing, provided the increase in emittance is due solely to diffusion. Since gold does not oxidize appreciably and has a low vapor pressure at 800°C the assumption is that the increase in emittance of the coating is due primarily to the diffusion of the gold into the base material. Figure 2 represents diffusion studies performed using NBS ceramic A418 and silicon monoxide as diffusion barriers. It can be seen from Figure 2 that these tests show silicon monoxide to be superior to A418 as a diffusion barrier. The bottom curve represents the emittance of a pure gold coating at 800°C which has not diffused. More diffusion studies are planned with these materials and with other diffusion barriers."

As the speeds of aerospace vheicles becomes greater, the need to protect instrument packages from heat will increase. Low emittance coatings offer a method of protection against heat transfer which is versatile and does not increase the weight and size of a vehicle.

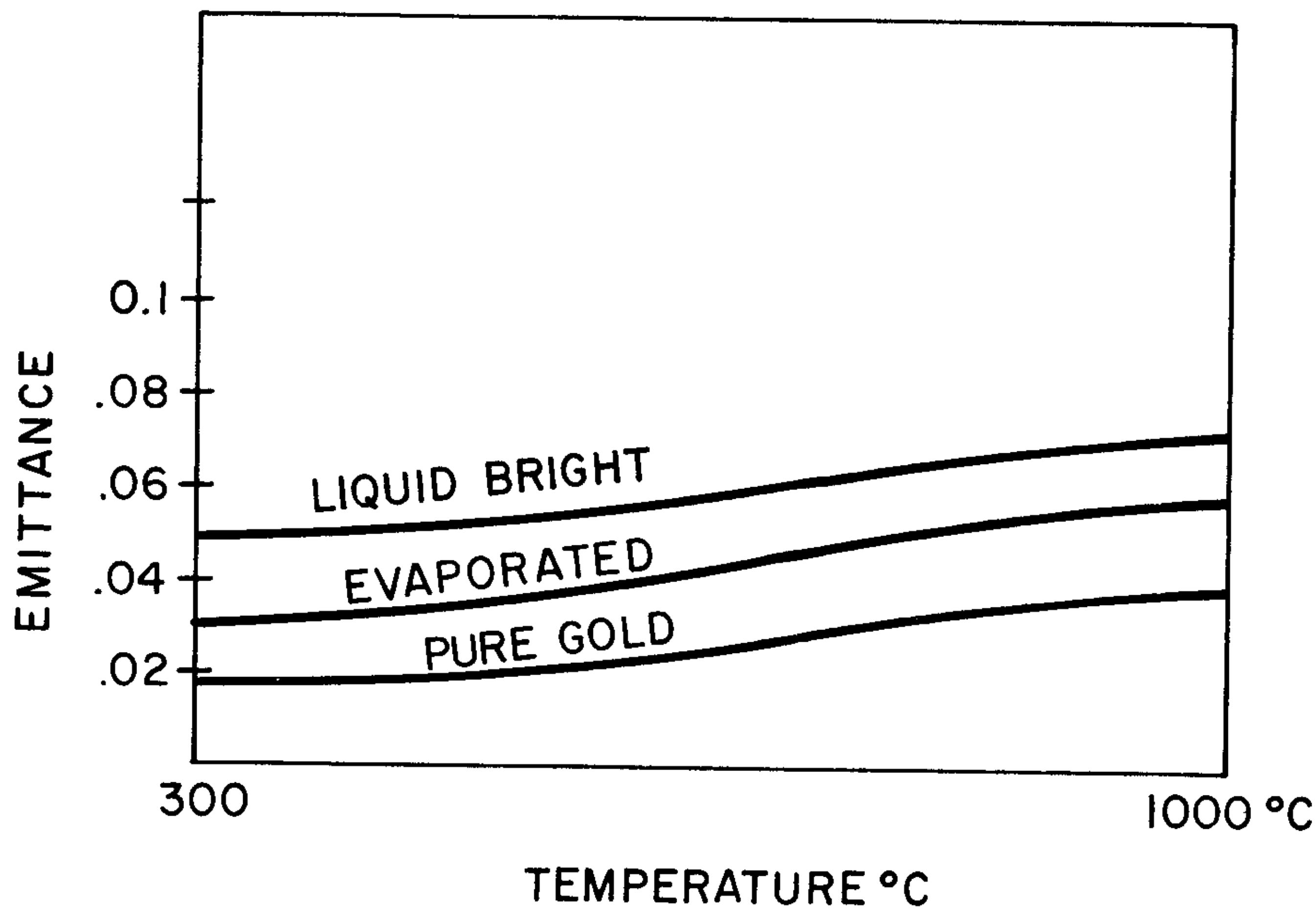

Figure 1 Emittance of Gold Coatings

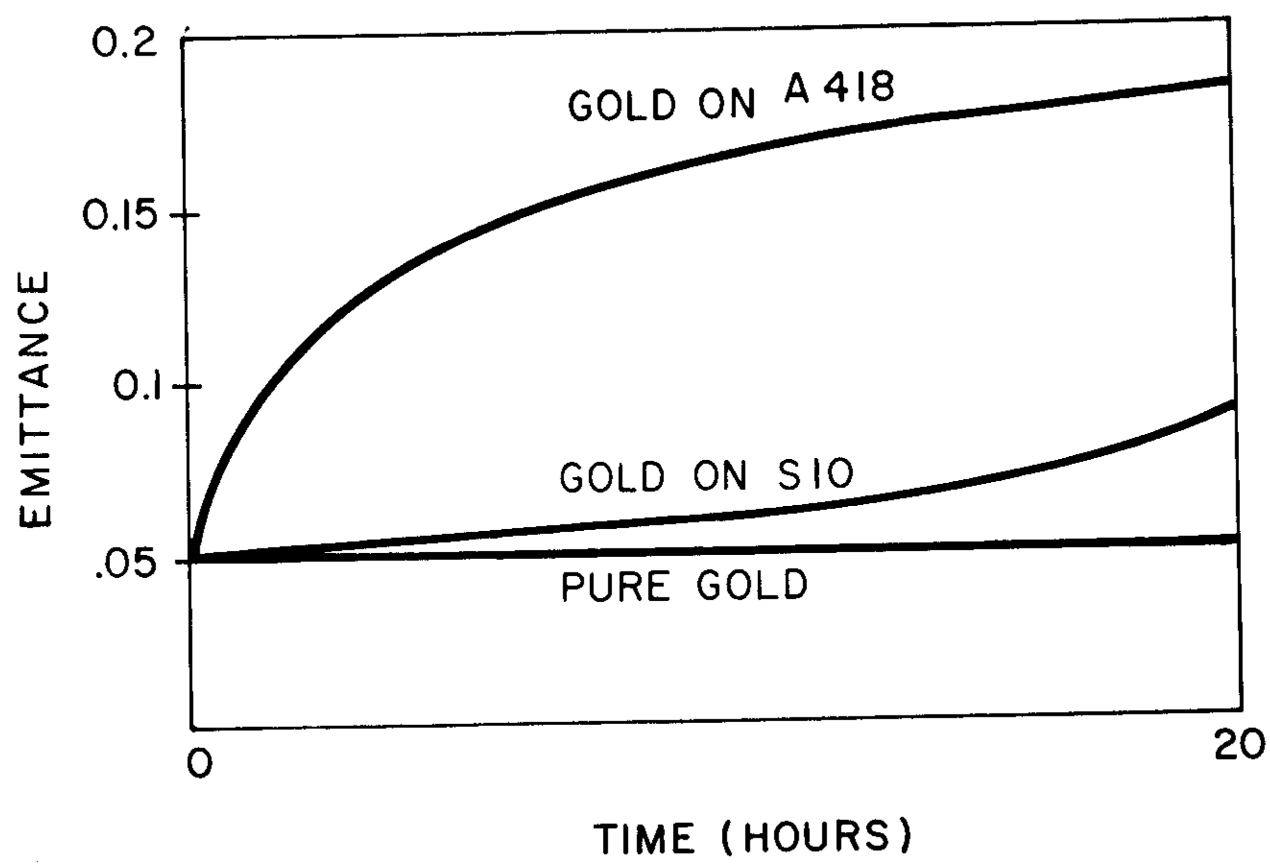

Figure 2 Effectiveness of Diffusion Barriers at 800°C